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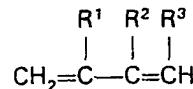
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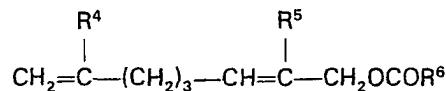
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(54) Catalytic process for 1-acyloxy-alkatrienes

(57) A method for the preparation of unsaturated esters containing at least 13 carbon atoms which comprises reacting a 1,3-diene of the formula:



wherein each of R<sup>1</sup> and R<sup>2</sup>, independently, represents hydrogen or alkyl and R<sup>3</sup> represents hydrogen, alkyl or alkenyl, with a non-conjugated dienol ester of the formula:



wherein each of R<sup>4</sup> and R<sup>5</sup> independently, represents hydrogen or alkyl, R<sup>6</sup> represents hydrogen, or an optionally substituted hydrocarbyl radical, in the presence of a rhodium or iridium compound and an organic halide of the formula:



wherein Q represents an optionally substituted alkenyl aralkyl, acyl or alkoxyethyl radical and X represents chlorine or bromine.

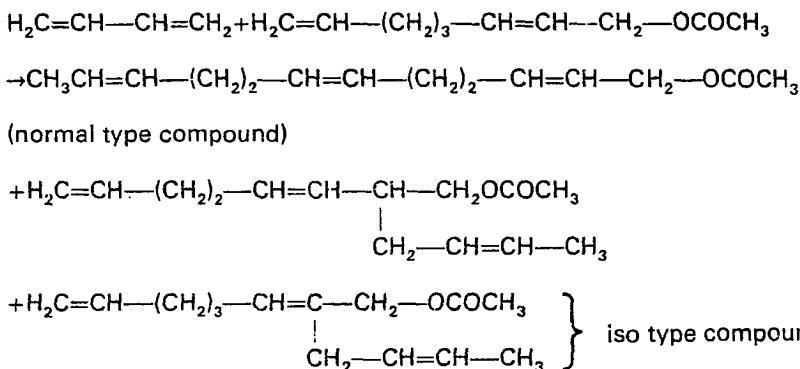
The products are useful intermediates in the manufacture of detergents.

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## SPECIFICATION Chemical process

This invention relates to a chemical process and more particularly to a method for the preparation of certain unsaturated esters.

- 5 It is already known from United Kingdom Patent Specification No. 1316725 to prepare  
unsaturated esters having the structure of oligomers of butadiene by reacting a conjugated diene with a  
1-acyloxy-2,7-alkadiene in the presence of a rhodium compound as catalyst. The reaction product  
contains a mixture of a straight chain compound which has been referred to as a "normal type  
compound" and branched chain compounds which have been referred to as "iso type compounds".  
10 Thus, the reaction between 1,3-butadiene and 1-acetoxy-2,7-octadiene may be represented as follows: 10



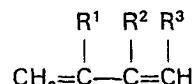
The ester products may be hydrolysed to alcohols which are useful in the preparation of surfactant materials.

- Japanese Patent Publication No. 75—13767 describes a process in which carbon tetrachloride or an alkylsilicon chloride is used to improve the activity of the rhodium catalyst. Similar organic halogen compounds, for example chloroform and dichloromethane are said not to have the same capacity to activate the rhodium catalyst.

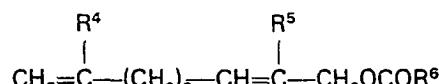
In Japanese Patent Publication No. 77—38533, it is shown that the activity of the aforementioned catalyst/co-catalyst system is still further improved by carrying out the reaction in the presence of hydrogen.

- It has now been found that certain halogen compounds as hereinafter defined are much more effective than carbon tetrachloride in promoting the activity of the rhodium catalyst, allowing the reaction to be performed more efficiently and at much lower rhodium levels.

Thus, according to the invention, there is provided a method for the preparation of unsaturated esters containing at least 13 carbon atoms which comprises reacting a 1,3-diene of the formula:



wherein each of R<sup>1</sup> and R<sup>2</sup>, independently, represents hydrogen or alkyl and R<sup>3</sup> represents hydrogen, alkyl or alkenyl, with a non-conjugated dienol ester of the formula:



35 wherein each of R<sup>4</sup> and R<sup>5</sup>, independently, represents hydrogen or alkyl and R<sup>6</sup> represents hydrogen or an optionally substituted hydrocarbyl radical, in the presence of a rhodium or iridium compound and an organic halide of formula:

$Q = x$

wherein Q represents an optionally substituted alkenyl aralkyl, acyl or alkoxyethyl radical and X represents chlorine or bromine.

- 40 The alkyl radicals which may be represented by  $R^1$  to  $R^5$  are preferably lower alkyl ( $C_1$ — $C_4$ ) radicals. Alkenyl radicals which may be represented by  $R^3$  preferably contain from two to four carbon atoms. Optionally substituted hydrocarbyl radicals represented by  $R^6$  include optionally substituted alkyl (especially lower alkyl), aralkyl, cycloalkyl and aryl radicals.

As examples of 1,3-dienes which may be used in the method of the invention, there may be

mentioned isoprene, piperylene, 1,3,7-octatriene and especially 1,3-butadiene.

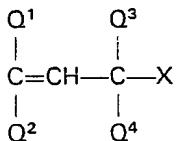
Non-conjugated dienol ester for use in the method of the invention may be prepared by a known method in which a butadiene is reacted with a carboxylic acid. Thus, reaction of 1,3-butadiene with a carboxylic acid such as acetic acid, propionic acid, pivalic acid or benzoic acid in the presence of a catalyst comprising palladium acetate and triarylphosphine or triaryl phosphite gives the corresponding 1-acyloxy-2,7-octadiene with some 3-acyloxy-1,7-octadiene. For use in the method of the invention, 1-acetoxy-2,7-octadiene is a particularly preferred component.

The rhodium or iridium compound employed as catalyst in the method of the invention may be an inorganic or organic salt or an organic complex. Examples of such compounds include rhodium trichloride, rhodium tribromide, rhodium nitrate, disodium hexachloroiridate, rhodium acetate, tetrakis( $\pi$ -allyl)dichlorodirhodium, tetrakis(ethylene)dichlorodirhodium, bis(cycloocta-1,5-diene)dichlorodirhodium and bis( $\pi$ -crotyl)tetrachloro(butadiene)dirhodium. Because of their superior catalytic activity, rhodium compounds are preferred to iridium compounds, rhodium trichloride being particularly useful. The rhodium or iridium compound may be added directly to the other components of the reaction mixture but is preferably used in the form of a solution in alcohol such as ethanol or in a hydrocarbon such as toluene.

The rhodium or iridium compound is suitably used in an amount of  $10^{-7}$  to  $10^{-1}$  gram-atom metal per mole of dienol ester.

As stated above, the organic halide used in the method of the invention is an optionally substituted alkenyl, aralkyl, acyl or alkoxyethyl chloride or bromide.

Suitable alkenyl halides include, in particular, compounds of the formula:



wherein each of  $Q^1$ ,  $Q^2$ ,  $Q^3$  and  $Q^4$ , independently, represents hydrogen, alkyl (especially lower alkyl), alkenyl or aryl and X is chlorine or bromine. Examples of suitable alkenyl halides include allyl chloride, allyl bromide, crotyl chloride, crotyl bromide, 1-chloro-2,7-octadiene, 3-chloro-1,7-octadiene and cinnamyl chloride.

Suitable aralkyl halides include benzyl chloride, benzyl bromide and  $\alpha,\alpha,\alpha$ -trichlorotoluene.

Suitable acyl halides include compounds of the formula:



wherein  $Q^5$  represents an optionally substituted alkyl, alkoxy, alkenyl or aryl radical (especially lower alkyl), lower alkoxy, lower alkenyl or phenyl and X is chlorine or bromine. Examples of suitable acyl halides of this type include acetyl chloride, chloroacetyl chloride, dichloroacetyl chloride, trichloroacetyl chloride, methyl chloroformate, acryloyl chloride, cinnamoyl chloride and benzoyl chloride. Other suitable acyl halides include cyanuric chloride and compounds of the formula:



wherein  $Q^6$  represents an optionally substituted alkyl or aryl radical and X is chlorine or bromine.

Suitable alkoxyethyl halides include chloromethyl methyl ether.

Particularly preferred organic halides for use in the method of the invention include cinnamyl chloride and crotyl chloride.

The organic halide is suitably used in an amount of 0.001 to 10 moles per mole of dienol ester.

The method of the invention may be performed by carrying out the reaction in a suitable reactor, for example an autoclave, at a temperature in the range 50°—250°C, preferably 100—130°C. The reaction may take place under autogenous pressure, and the reactants may be used in bulk or in the form of solutions in suitable solvents.

It is a feature of the method of the invention that a higher reaction rate (expressed as moles dienol ester converted per gram-atom of rhodium or iridium per hour) may be achieved than when carbon tetrachloride is used as the promoter as described in the prior art.

A further significant increase in the reaction rate may be achieved by performing the reaction in the presence of chromium or a chromium compound in addition to the rhodium or iridium compound and the organic halide. Suitable sources of chromium include chromium metal itself and chromium-containing alloys. Thus, an increase in the reaction rate may be effected by carrying out the reaction in a stainless steel reaction vessel. Suitable chromium compounds which may be added to the reaction mixture include inorganic chromium salts, for example anhydrous chromic chloride and especially hydrated chromic chloride.

The reaction may also be promoted by hydrogen gas. Thus, it is advantageous to carry out the reaction in the presence of hydrogen at a pressure of 0.1 to 100 atmospheres, preferably 10 to 15 atmospheres. If desired, a combination of hydrogen and chromium or a chromium compound may be used.

5 The products obtained by the method of the invention are useful as chemical intermediates. In particular, they may be converted by hydrolysis and hydrogenation into saturated higher alcohols which are useful in the manufacture of detergents and other surfactant materials.

The invention is illustrated but not limited by the following Examples. The acetoxyoctadiene used in Examples 1—10 and 13 was a mixture consisting of 95—96% 1-acetoxy-2,7-octadiene and 4—5% 10 3-acetoxy-1,7-octadiene.

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#### EXAMPLE 1

To 3.5 g (21 mmol) acetoxyoctadiene in a strong-walled glass tube equipped with a pressure resistant Teflon valve were added 0.2 ml of a solution of RhCl<sub>3</sub> in ethanol (0.002 mg-atom Rh), 20 mmol of one of the organic halides listed in Table 1, and 0.35 g dodecane as g.l.c. standard. The mixture 15 was then cooled to —20°C and 1,3-butadiene (3 ml) was condensed in. The tube was sealed and heated on an oil bath at 110°C for 1 hour with magnetic stirring.

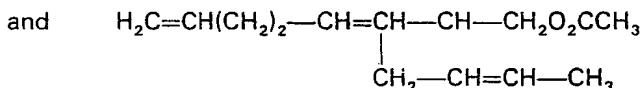
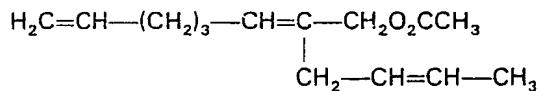
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The results vary with the organic halide and are collected in Table 1. The catalytic activity in these reactions and the following Examples is described by the turnover number in moles converted acetoxyoctadiene per g-atom Rh per hour.

20 G.I.c. analysis showed that the reaction products consisted mainly of two groups of compounds which were separated by preparative g.l.c. using a 5 ft. column of 10% Apiezon L on supelcopor. The lower boiling product component was a mixture of at least two isomers. The mass spectrum showed a molecular ion (m/e 276, C<sub>12</sub>H<sub>19</sub>O<sub>2</sub>CCH<sub>3</sub>) and loss of acetic acid (m/e 216) as well as loss of a crotyl radical (m/e 221). The N.M.R. spectrum identified the compound as a mixture of two known 1-acetoxy-25 2-butenyloctadienes of the structures:

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The higher boiling component gave an essentially identical mass spectrum and an NMR spectrum which was identical to that of the known compound 1-acetoxy-2,6,10-dodecatriene (normal type compound).

TABLE 1

| Run No. | Acetoxy-octadiene (mmol) | RhCl <sub>3</sub> (mmol) | halocarbon activator                    | Conversion (%) *1 | n/iso ratio *2 | sel (%) *3 | turnover no. |
|---------|--------------------------|--------------------------|---|-------------------|----------------|------------|--------------|
| 1       | 20.9                     | 0.002                    | CH <sub>3</sub> COCl                    | 92                | 1.3            | 94         | 9600         |
| 2       | 21.0                     | 0.002                    | PhCH=CHCH <sub>2</sub> Cl               | 89                | 1.3            | 96         | 9345         |
| 3       | 21.0                     | 0.002                    | H <sub>2</sub> C=CHCOCl                 | 66                | 1.2            | 99         | 6930         |
| 4       | 20.8                     | 0.002                    | PhCH=CHCOCl                             | 60                | 1.0            | 100        | 6250         |
| 5       | 20.8                     | 0.002                    | cyanuric chloride                       | 60                | 1.4            | 100        | 6240         |
| 6       | 20.9                     | 0.002                    | PhCCl <sub>3</sub>                      | 50                | 1.5            | 100        | 5230         |
| 7       | 21.2                     | 0.002                    | CICOOCH <sub>3</sub>                    | 46                | 1.1            | 100        | 4880         |
| 8       | 20.7                     | 0.002                    | CH <sub>2</sub> =CHCH <sub>2</sub> Cl   | 68                | 1.2            | 99         | 7045         |
| 9       | 21.2                     | 0.002                    | CH <sub>3</sub> CH=CHCH <sub>2</sub> Cl | 84                | 1.2            | 99         | 9000         |
| 10      | 21.4                     | 0.002                    | CH <sub>2</sub> =CHCH <sub>2</sub> Br   | 16                | 0.6            | 100        | 1660         |
| 11      | 21.0                     | 0.002                    | CICH <sub>2</sub> COCl                  | 15                | 1.6            | 100        | 1560         |
| 12      | 20.9                     | 0.002                    | Cl <sub>3</sub> CCOCl                   | 9                 | 1.5            | 100        | 940          |

\*1— conversion of 1-acetoxy-2,7-octadiene.

\*2 — ratio of normal type-compound produced to iso type-compound produced.

\*3 — selectivity of reaction products comprising normal type-compound and iso-type compound.

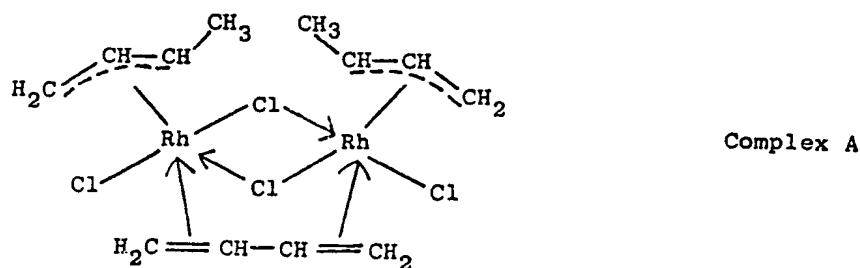
The crude reaction product can be hydrogenated without prior isolation of the C<sub>12</sub> acetates, preferably using 10% palladium on charcoal under 1 atm. H<sub>2</sub> at 50—60°C. The resulting saturated alkyl acetates are easily hydrolysed by NaOH in 95% methanol to give a mixture of n-dodecanol and 2-butyl octan-1-ol which can be separated by g.l.c. and identified by mass spectrometry and comparison with authentic samples.

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**EXAMPLE 2**

The same procedure as in Example 1 was employed, with the exception that the catalyst was a 0.005 molar toluene solution of the dimeric rhodium crotyl complex Rh<sub>2</sub>Cl<sub>2</sub>(μ-Cl)<sub>2</sub>( $\pi$ -C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>(C<sub>4</sub>H<sub>6</sub>). (Complex A). The reaction mixture was analysed by g.l.c. using dodecane as standard. The results are collected in Table 2.

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**EXAMPLE 3**

The same method as in Example 1 was followed for reacting 3.64 g (21.6 mmol) acetoxy-octadiene with 1,3-butadiene (3 ml) in the presence of 3.05 g (20 mmol) cinnamyl chloride, but employing a solution of 0.49 mg (0.001 mmol) [(COD)RhCl]<sub>2</sub> (COD = 1,5-cyclooctadiene) in 0.2 ml toluene. After 1 hour at 110°C, 30% of the acetoxy-octadiene was converted to normal and iso type C<sub>12</sub> compounds in 100% selectivity. The n/iso ratio was 1.3 and the turnover number 3260 moles per g-atom Rh per hour. (analysis by g.l.c.).

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TABLE 2

| Run No. | Acetoxy-octadiene (mmol) | Rh complex A (mmol) | halocarbon activator    | Conversion (%) | n/iso ratio | sel (%) | turnover no. |
|---------|--------------------------|---------------------|-------------------------|----------------|-------------|---------|--------------|
| 1       | 21.2                     | 0.001               | CH <sub>3</sub> COCl    | 76             | 1.3         | 100     | 8060         |
| 2       | 21.5                     | 0.001               | CH <sub>2</sub> =CHCOCl | 56             | 1.4         | 100     | 6030         |
| 3       | 21.2                     | 0.001               | PhCOCl                  | 53             | 1.3         | 100     | 5570         |
| 4       | 21.1                     | 0.001               | PhCH=CHCOCl             | 43             | 0.9         | 100     | 4550         |
| 5       | 20.9                     | 0.001               | CICH <sub>2</sub> COCl  | 13             | 1.5         | 100     | 1340         |
| 6       | 21.1                     | 0.001               | Cl <sub>3</sub> CCOCl   | 10             | 1.5         | 100     | 1020         |

TABLE 3

| Run No. | Acetoxy-octadiene (mmol) | Rh complex A (mmol) | Chromium compound added                 | Conversion (%) | n/iso ratio | sel (%) | turnover no. |
|---------|--------------------------|---------------------|---|----------------|-------------|---------|--------------|
| 1       | 41.7                     | 0.001               | —                                       | 36             | 1.3         | 100     | 7550         |
| 2       | 42.2                     | 0.001               | CrCl <sub>3</sub> .6H <sub>2</sub> O 1g | 65             | 1.2         | 100     | 13660        |
| 3       | 41.9                     | 0.001               | Cr powder 0.5 g                         | 61             | 1.2         | 99      | 12710        |

**EXAMPLE 4**

The same method as in Example 1 was followed for reacting 7.1 g (42 mmol) acetoxyoctadiene with 1,3-butadiene (6 ml) for 1 hour at 110°C in the presence of 3.05 mg (20 mmol) cinnamyl chloride and 0.001 mmol Rh<sub>2</sub>Cl<sub>4</sub>( $\pi$ -C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>(C<sub>4</sub>H<sub>6</sub>) (complex A) in 0.2 ml toluene.

- 5 In two similar reactions, CrCl<sub>3</sub>·6H<sub>2</sub>O (1.0 g) and chromium metal powder (0.5 g), respectively, 5 were added to the reaction mixture before heating. The results are collected in Table 3.

**EXAMPLE 5**

Liquefied 1,3-butadiene (18 ml, ca. 200 mmol) was added at -20°C to 16.6 g (98.6 mmol) acetoxyoctadiene in the presence of 0.001 mmol Complex A in 0.2 ml toluene (0.002 mg-atom Rh), 10 1.45 g dodecane (g.l.c. standard) and 2.52 g (16.5 mmol) cinnamylchloride. The mixture was heated for 10 2 hours at 120°C under 150 psi H<sub>2</sub>. The conversion of acetoxyoctadiene of 60% corresponds to a turnover number of 14800 per hour. The selectivity to C<sub>12</sub> products was 99.5%, n/iso ratio 1.4.

**EXAMPLE 6**

The same method as for Example 5 was followed for reacting 16.87 g (100.3 mmol) acetoxyoctadiene with 1,3-butadiene (18 ml) in the presence of 0.002 mmol RhCl<sub>3</sub> in 0.2 ml ethanol, 15 2.0 g, CrCl<sub>3</sub>·6H<sub>2</sub>O, 2.52 g (16.5 mmol) cinnamyl chloride and 1.30 g dodecane under 150 psi H<sub>2</sub> at 120°C for 2 hours. Conversion was 67%, selectivity to C<sub>12</sub> products 100%, n/iso ratio 1.2, the turnover number 16,650.

**EXAMPLE 7**

20 The same method as for Example 5 was followed for reacting acetoxyoctadiene with 1,3-butadiene (18 ml) for 2 hours at 120°C in the presence of 0.001 mmol Complex A in 0.2 ml toluene, 20 2 g CrCl<sub>3</sub>·6H<sub>2</sub>O, dodecane (ca. 1.6 g), 150 psi H<sub>2</sub> pressure and varying amounts of cinnamyl chloride. The results are collected in Table 4.

**EXAMPLE 8**

25 The same method as for Example 5 was followed for reacting acetoxyoctadiene with 1,3-butadiene (18 ml) for 2 hours at 120°C in the presence of complex A (0.001 mmol,  $\leq$ 0.002 mg-atom Rh) in 0.2 ml toluene, dodecane (1.60 g), CrCl<sub>3</sub>·6H<sub>2</sub>O (2.0 g) under 150 psi H<sub>2</sub> and with different types of halocarbon additives. The results are collected in Table 5. 25

**EXAMPLE 9**

30 The same method as for Example 5 was followed for reacting 16.8 g (100 mmol) acetoxyoctadiene with 18 ml 1,3-butadiene in the presence of 0.002 mmol RhCl<sub>3</sub> in 0.2 ml ethanol and 30 9.0 g (100 mmol) crotyl chloride. The reaction was carried out under 200 psi hydrogen in an autoclave where the reaction mixture had contact with stainless steel containing 17—20% Cr. After 2½ hours at 105°C, 68% of the acetoxyoctadiene was converted to C<sub>12</sub> acetate isomers in 99% selectivity (n/iso 35 ratio 1.3). The turnover number was 15450/hour. 35

**EXAMPLE 10**

The same method as in Example 1 was followed for reacting 7.35 g (40.31 mmol) propionoxyoctadiene (consisting of 93% 1-propionoxy-2,7-octadiene and 7% 3-propionoxy-1,7-octadiene) with 6 ml 1,3-butadiene in the presence of 0.002 mmol RhCl<sub>3</sub> in 0.2 ml ethanol, 0.1 g CrCl<sub>3</sub>·6H<sub>2</sub>O, 3.05 g (20 mmol) cinnamyl chloride and 0.773 g dodecane. After 1 hour at 100°C, the conversion was 31%, the selectivity to C<sub>12</sub> propionates 100%, the n/iso ratio 1.1 and the turnover number 6250. 40

**EXAMPLE 11**

45 The same method as for Example 1 was followed for reacting 8.53 g (40.6 mmol) 1-pivaloxy-2,7-octadiene with 6 ml 1,3-butadiene in the presence of 0.002 mmol RhCl<sub>3</sub> in 0.2 ml ethanol, 3.05 g (20 mmol) cinnamyl chloride and 0.1 g CrCl<sub>3</sub>·6H<sub>2</sub>O. After 1 hour at 110°C, the conversion was 5%, the selectivity 99% and the turnover number 1000. 45

TABLE 4

| Run No. | C <sub>8</sub> H <sub>13</sub> OAc (mmol) | Cinnamyl Chloride (mmol) | Conversion (%) | n/iso ratio | sel (%) | turnover no. |
|---------|---|--------------------------|----------------|-------------|---------|--------------|
| 1       | 99.7                                      | 0                        | 30             | 1.5         | 99.5    | 7550         |
| 2       | 99.0                                      | 0.22                     | 37             | 1.1         | 100     | 9100         |
| 3       | 100.1                                     | 1.0                      | 53             | 1.2         | 99      | 13320        |
| 4       | 100.0                                     | 2.46                     | 60             | 1.3         | 98      | 14930        |
| 5       | 101.4                                     | 10                       | 67             | 1.2         | 98      | 17040        |
| 6       | 98.8                                      | 20                       | 85             | 1.2         | 97      | 20940        |

TABLE 5

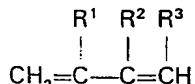
| Run No. | C <sub>8</sub> H <sub>13</sub> OAc (mmol) | Rh complex A (mmol) | halocarbon (mmol)      | Conversion (%) | n/iso ratio | sel (%) | turnover no. |
|---------|---|---------------------|------------------------|----------------|-------------|---------|--------------|
| 1       | 99.7                                      | 0.001               | —                      | 30             | 1.5         | 99.5    | 7550         |
| 2       | 101.2                                     | 0.001               | crotyl chloride 20     | 56             | 1.3         | 99      | 14090        |
| 3       | 101.7                                     | 0.001               | acetyl chloride 27     | 73             | 1.1         | 100     | 18540        |
| 4       | 98.8                                      | 0.001               | cinnamyl chloride 16.5 | 85             | 1.2         | 97      | 20940        |

## EXAMPLE 12

The same method as for Example 1 was followed for reacting 6.81 g (40.5 mmol) acetoxyoctadiene with 7 ml 1,3-butadiene in the presence of 56 mg (0.1 mol)  $\text{Na}_2\text{IrCl}_6 \cdot n\text{H}_2\text{O}$ , 0.5 ml ethanediol and 1.9 g (21 mmol) crotyl chloride. After heating the mixture for 2 hours at 110°C the conversion was 65%, the n/iso ratio 1.7, the selectivity to  $C_{12}$  acetates 99% and the turnover number 113.

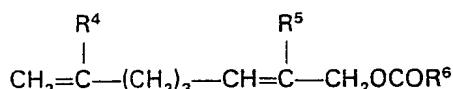
## CLAIMS

1. A method for the preparation of unsaturated esters containing at least 13 carbon atoms which comprises reacting a 1,3-diene of the formula:



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wherein each of  $\text{R}^1$  and  $\text{R}^2$ , independently, represents hydrogen or alkyl and  $\text{R}^3$  represents hydrogen, alkyl or alkenyl, with a non-conjugated dienol ester of the formula:



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15 wherein each of  $\text{R}^4$  and  $\text{R}^5$  independently, represents hydrogen or alkyl,  $\text{R}^6$  represents hydrogen, or an optionally substituted hydrocarbyl radical, in the presence of a rhodium or iridium compound and an organic halide of the formula:



wherein Q represents an optionally substituted alkenyl aralkyl, acyl or alkoxyethyl radical and X represents chlorine or bromine.

20 2. A method according to claim 1 substantially as hereinbefore described with reference to the foregoing Examples.

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